

SHALLOW AND DEEP CORE LEVEL IONIC FRAGMENTATION OF THE CCl₄ MOLECULE

A. C. F. Santos¹, J. B. Maciel¹, M. M. Sant'Anna², K. T. Lung⁴, J. Cotter⁵, W. Stolte³, and G. G. B. de Souza¹

¹Instituto de Química, Universidade Federal do Rio de Janeiro, Brazil

²Pontifícia Universidade Católica do Rio de Janeiro, Brazil

³Advanced Light Source, Berkeley, CA, USA

⁴University of Waterloo, Canada

⁵University of Nevada, Reno, USA

Carbon tetrachloride, CCl₄, is a volatile compound with several important technological applications, being for instance used as an etching agent in microelectronics. In addition, the CCl₄ molecule pollutes atmosphere harmfully and has been related to the so-called greenhouse effect [4]. Several studies have been dedicated to the photoabsorption spectrum of the CCl₄ molecule, both in the valence and inner-shell regions [1-4]. This molecule presents a tetrahedral symmetry (T_d point group).

In this work we report on the ionic fragmentation of the CCl₄ molecule following valence, and core level photoexcitation, using tunable synchrotron radiation as exciting source. Branching ratios for the ionic fragments have been determined, as a function of the incident photon energy around the valence, Cl 2*p* edge (~200 eV), C 1*s* continuum (~300 eV), and Cl 1*s* (~2800 eV) regions.

The valence and shallow core levels (Cl 2*p* and C 1*s*) measurements were performed at the Center for Advanced Microstructures and Devices (CAMD), Louisiana, USA. The experimental set up has been described recently [5]. Basically, light from a toroidal grating monochromator (TGM) beamline intersected an effusive gaseous sample inside a high vacuum chamber, with base pressure in the 10⁻⁸ torr range. PEPICO and PIPICO data were determined as a function of the photon energy using a time-of-flight mass spectrometer.

The second part of this work (deep core level ionization) was performed using x-ray synchrotron radiation from beamline 9.3.1 at the Advanced Light Source (ALS) in Berkeley, California. 9.3.1 is a bending magnet beamline covering 2-6 keV photon-energy range. This beamline provides a flux of 10¹¹ photons s⁻¹ in a bandpass ≤ 0.5 eV. Photon-energy calibration was achieved by scanning the monochromator through the Cl K-edge region while monitoring the total-ion yield. The photon-energy was determined with 0.2 eV accuracy. Figs. 1 and 2 show the PEPICO mass spectra of CCl₄ around the Cl 2*p* and Cl 1*s* edges.

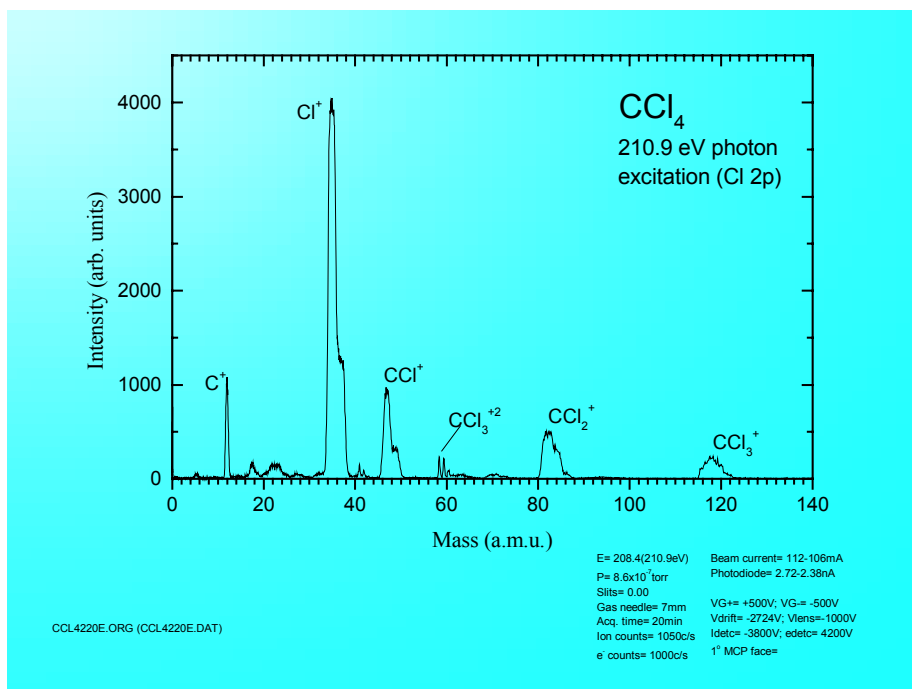


Fig 1. - Mass Spectrum of CCl₄ molecule near the Cl 2p edge (210 eV).

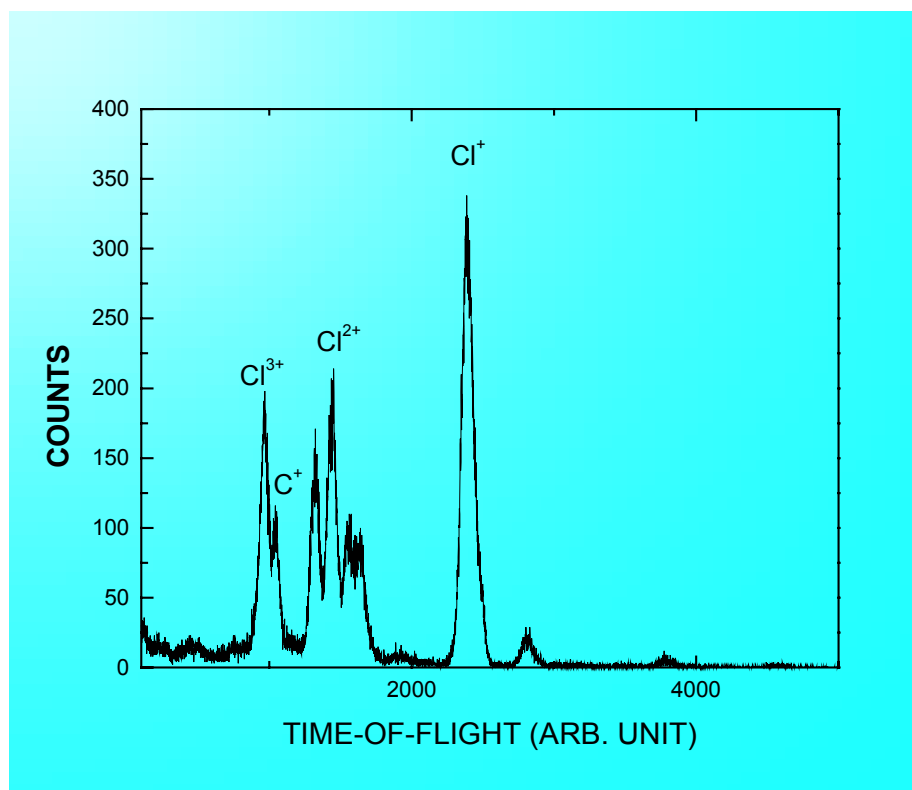


Fig.2 – Mass spectrum of CCl₄ molecule around Cl 1s edge.

There is no evidence for stable CCl_4^+ ion in the energy range studied in this work in accordance with earlier studies using electron impact technique [6, 7]. The first evidence for metastable CCl_4^+ ion was given by Drewello *et al.* [8], with lifetimes in the order of 10^{-5} s. According to Kaufmann *et al.* [8], the CCl_4^+ is not observed because the excitation of the carbon tetrachlorine molecule occurs into a repulse excited state of neutral CCl_4 which dissociates into Cl and CCl_3 that in turns, autoionizes giving rise to CCl_3^+ ion. Leiter *et al.* [6] observed the metastable dissociation of CCl_4^{+*} into CCl_3^+ and Cl, avoiding the postulation of dissociation of neutral CCl_4 prior to ionization.

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Principal investigator: Gerardo Gerson B de Souza, Instituto de Química, Universidade Federal do Rio de Janeiro. E-mail: gerson@iq.ufRJ.br. Telephone: (55) 021 2590-9024.